PATENT SPECIFICATION (11) 1291761

1291761

DRAWINGS ATTACHED

(21) Application No. 2096/70 (22) Filed 15 Jan. 1970

(45) Complete Specification published 4 Oct. 1972

(51) International Classification C04B 35/00

(52) Index at acceptance C1J 12 17 19 2 28 34 4

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(54) PIEZOELECTRIC CERAMIC COMPOSITIONS

(71) We, RION KABUSHIKI KAISHA, of No. 24—41 Higashi-motomachi 3-chome, City of Kokubunji, Tokyo, Japan, a body corporate organized and existing under the Laws of Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to improvements in piezoelectric ceramic compositions suitable for use as electromechanical transducers.

There is already known a wide variety of piezoelectric ceramic compositions, for example, the composition may be a one-component system comprising barium titanate ($BaTiO_3$) or potassium metaniobate ($KNbO_3$), which have the perovskite structure, lithium metaniobate ($LiNbO_3$), which has the ilmenite structure, or lead metaniobate ($PbNbO_3$), which has the tungsten bronze structure. Alternatively, the composition may be a binary system, such as lead zirconate titanate composed of $PbZrO_3$ and $PbTiO_3$ effectively in solid solution and having the perovskite structure. This lead zirconate titanate has had its electromechanical coupling improved by partly replacing the lead by bivalent strontium (Sr^{II}), calcium (Ca^{II}) or barium (Ba^{II}), which have substantially the same ion radius as lead.

Recently, there have been proposed piezoelectric ceramic compositions in the form of a ternary system including the abovementioned lead zirconate titanate and having added thereto $Pb(Nb_{2/3}Co_{1/3})O_3$ or $Pb(Nb_{2/3}Mg_{1/3})O_3$ having the composite perovskite structure. In addition, lead barium zirconate titanate

$PbZrO_3$—$PbTiO_3$—$BaZrO_3$—$BaTiO_3$,

a quaternary system, has been reported in an article by T. Ikeda entitled "Studies on (Ba—Pb)(Ti—Zr)O_3 System", in the Journal of the Physical Society of Japan, Vol. 14, page 168 (1959). This lead barium zirconate titanate is the first known quaternary system for a piezoelectric ceramic composition. This known quaternary system is composed essentially of four components having identical crystallographic structures.

The present invention consists in a piezoelectric ceramic composition in the form of a solid solution containing only the components: (1) from 30 to 60 mol % of lead titanate, alone or in admixture with an up to equimolar amount of lead stannate; (2) from 40 to 70 mol % of lead zirconate, alone or in admixture with an up to equimolar amount of lead stannate, components (1) and (2) totalling 100 mol %; (3) from 1 to 30 mol % of PbO, CaO, SrO, BaO or CdO or a mixture thereof; and (4) from 1 to 15 mol % of Nb_2O_5, Ta_2O_5 or Bi_2O_5 or a mixture thereof; the percentages of components (3) and (4) being based on the total of components (1) and (2).

When components (3) and (4)—the oxide and pentoxide—are combined in certain special mol ratios, they may be considered to form a single component of formula $A_mMO_{(2.5+m)}$, where m is 0.25, 0.1, 0.75, 1.00, 1.25 or 1.50. Therefore, the invention also provides a piezoelectric ceramic composition in the form of a solid solution containing only the components: (1) from 30 to 60 mol % of lead titanate, alone or in admixture with an up to equimolar amount of lead stannate; (2) from 25 to 65 mol % of lead zirconate, alone or in admixture with an up to equimolar amount of lead stannate; and (3) from 1 to 30 mol % of a compound of general formula $A_mMO_{(2.5+m)}$, where A is Pb^{II}, Ca^{II}, Sr^{II}, Ba^{II} or Cd^{II}, M is Nb^{V}, Ta^{V} or Bi^{V} and m is 0.25, 0.5, 0.75, 1.00, 1.25 or 1.50, components (1), (2) and (3) totalling 100 mol %.

Electromechanical transducers using piezoelectric ceramic compositions are well known in the art as to their construction and mode of operation.

The conventional multi-component systems of piezoelectric ceramic compositions, such as previously described, suitable for use in electromechanical transducers all have been composed of components having the same crystallographic structure. However, the invention is based upon the discovery that the combination

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of lead zirconate titanate ($PbZrO_3$—$PbTiO_3$) of the perovskite structure with one or two components different in crystallographic structure therefrom leads to improvements in the coefficient of electromechanical coupling or planar coupling and in the dielectric constant.

The piezoelectric ceramic compositions according to the invention are quite different in composition from the conventional ones and may be expressed by the general formula:

$$aPbTiO_3+bPbZrO_3+cAO+dM_2O_5 \quad (1)$$

where A and M have the same meanings as above and where the $PbTiO_3$ and/or the $PbZrO_3$ may be partly replaced by $PbSnO_3$.

In the above formula (1) the coefficients *a*, *b*, *c* and *d* designate the molar percentages of the associated components formed into a solid solution. Thus, *a* ranges from 30 to 60% and *b* ranges from 40 to 70% with a+b=100%. Coefficients *c* and *d* in the third and fourth terms range respectively from 1 to 30% and from 1 to 15%, based upon the total moles of lead titanate and lead zirconate, or the mixtures of lead titanate and lead zirconate with lead stannate.

The following discussion of the invention is primarily directed to the case in which the third and fourth components are lead oxide and niobium pentoxide, respectively. It will, of course, be understood that the lead and the niobium may be replaced by any one of the other equivalent elements listed above. Selecting, then, lead and niobium as the elements "A" and "M" respectively, formula (1) can be rewritten as:

$$aPbTiO_3+bPbZrO_3+cPbO+dNb_2O_5 \quad (1')$$

That is, the compositions expressed by the formula (1') have, in addition to the principal components, lead titanate ($PbTiO_3$) and lead zirconate ($PbZrO_3$), lead oxide (PbO) and niobium pentoxide (Nb_2O_5) combined with the principal components. Lead titanate and lead zirconate have the perovskite structure while lead oxide and niobium pentoxide have different crystallographic structures from the principal components.

If lead monoxide (PbO) and niobium pentoxide (Nb_2O_5) are combined in certain molar ratios with each other then the oxides can be considered to form together a single component, expressed as $Pb_mNbO_{(2.5+m)}$ where *m* is 0.25. 0.50, 0.75, 1.00, 1.25 or 1.50. For example, putting *m*=0.5 provides lead metaniobate ($Pb_{0.5}NbO_3$ or $PbNb_2O_6$) having the tungsten bronze structure and putting *m*=1.0 provides lead pyroniobate ($Pb_2Nb_2O_7$ or $PbNbO_{3.5}$) having the pyrochlore structure. These materials themselves are known as ferroelectric materials and disclosed, for example, by R. S. Roth in "Phase Equilibrium Relations in the Binary System Lead oxide-Niobium Pentoxide", Journal of Research of National Bureau of Standards, Vol. 62, page 27 (1959).

Under these circumstances, the formula (1) can be transformed into the following formula:

$$a'PbTiO_3+b'PbZrO_3+c'Pb_mNbO_{(2.5+m)} \quad (2)$$

where *a'*, *b'* and *c'* designate the molar percentages of the associated components and *m* has the same value as above. Those compositions of formula (2) are, of course, within the scope of the invention as a specific form. In other words that form of the invention expressed by the formula (a) includes a binary system (lead titanate-lead zirconate) having the perovskite structure having added thereto a tertiary component composed of lead oxide-niobium pentoxide having the tungsten bronze or pyrochlore structure to form a ternary system composition into a solid solution.

It has been found that the piezoelectric compositions in the form of a ternary system consisting, by molar ratio, essentially of from 30 to 60% of lead titanate, from 25 to 65% of lead zirconate and from 1 to 30% of a component $PbNbO_{(2.5+m)}$ with the three components formed into a solid solution having unexpectedly improved physical properties, such as planar coupling coefficient k_p and dielectric constant ϵ.

It has also been found that bivalent lead forming part of the third component of formula (2) may be wholly or partly replaced by any one of bivalent calcium (Ca^{II}), strontium (Sr^{II}), barium (Ba^{II}) or cadmium (Cd^{II}), which are substantially equal in ion radius to the bivalent lead. Similarly pentavalent niobium (Nb^{V}) may be wholly or partly replaced by either pentavalent tantalum (Ta^{V}) or bismuth (Bi^{V}). It has been further found that either or both of titanium (Ti) and zirconium (Zr) may be partly replaced by tin (Sb).

Therefore the compositions in the form of a ternary system can be expressed by the general formula

$$a'PbTiO_3+b'PbZrO_3+c'A_mMO_{2.5+m} \quad (2')$$

where A, M and *m* have the same meanings as above and the coefficients *a'*, *b'* and *c'* range from 30 to 60 mol %, from 25 to 65 mol % and from 1 to 30 mol %, respectively, *a'*, *b'* and *c'* totalling 100 mol %.

In the ternary systems above described, the proportions of AO and M_2O_5 forming the tertiary component $A_mM_2O_{2.5+m}$ are subject to some limitations. However, it has been found that AO and M_2O_5 can be satisfactorily combined in any desired proportion with each

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other within certain limits. This results in the quaternary system as expressed by the general formula (1).

The compositions disclosed herein may be prepared in accordance with various ceramic procedures which in themselves are well known in the art. With lead (Pb) and niobium (Nb), for example, selected as the A and M elements set forth in the formula (1) or (2'), a preferred method involves the use of lead oxide (PbO), niobium pentoxide (Nb_2O_5), titania (TiO_2) and zirconia (ZrO_2) all of a relatively pure grade (e.g. C.P. grade) combined in the desired proportions. The starting materials are intimately mixed in a small ball mill for from 1 to 1.5 hours. The resulting mixture is then calcined in a suitable furnace, such as a Barch furnace, at a temperature of from 880°C to 890°C and is thereafter maintained at the calcining temperature for one hour. The calcined material is finely pulverized in a small ball mill for about one hour and the finely pulverized material is then mixed with a suitable binder, such as a 7% solution of polyvinyl alcohol in an amount of about 8% based upon the weight of the pulverized material. The resulting mixture can be pressed in a suitable mould under a pressure of 2400 kg/cm² to form it into the desired shape and dimensions. The bodies thus formed are sintered in a suitable furnace, such as a Barch furnace, at a temperature of from 1200° to 1300°C depending on the particular composition and are then maintained at the sintering temperature for a period of from 1.5 to 2 hours.

In order to prevent the lead contained in the starting materials from vaporizing in either the calcining or the sintering process, it is preferred to process the material within a crucible of sintered magnesia of high purity and particularly to effect sintering in an atmosphere including a sufficient amount of lead vapour. The final products obtained by these means were found by chemical analysis to be substantially free from loss of lead.

To demonstrate the effectiveness of the invention, the method described above was used to prepare disc-shaped ceramic bodies having a diameter of from 21 to 21.7 millimeters dependent upon the composition and a thickness of 2 millimeters. A silver paint was applied to the opposite main faces of each ceramic body and baked at about 700°C to provide the respective electrodes on the opposite faces. While the ceramic bodies might be electrostatically polarized in any desired manner they could be effectively subjected to successive electrostatic polarizations in three separate vessels filled with a silicone oil at different temperatures such that the polarization was first effected at 200°C for 5 minutes in a first vessel, then at 100°C for 5 minutes in the second vessel and finally at room temperature for 5 minutes in the third vessel with the ceramic bodies always put in a polarizing electric field of 25 Kilovolts per centimeter. Thus the polarization time totalled 15 minutes. This measure serves to reduce a time period for which the ceramic body is continuously put in the electric field while its temperature decreases from its high magnitude to room temperature. In addition it was found that for each triad of ceramic bodies identical in composition to one another and electrostatically polarized in the manner described above, the measured magnitudes of physical constants as will be subsequently described varied from one another only within 5%.

The dielectric constant ϵ of each ceramic body was determined from its capacitance, measured using the well known bridge method.

In order to determine the planar coupling coefficient k_p of each body, the constant voltage method, well known in this art, was used to determine the resonance frequency f_R and antiresonance frequency f_A thereof. Then the planar coupling k_p in the radial direction of the disc was calculated from accordance with the equation

$$k_p^2 = \frac{1}{p}\frac{f_A^2 - f_R^2}{f_A^2}$$

where

$$P = \frac{2(1+\sigma^E)}{\eta 1 - [1-(\sigma^E)^2]}$$

In the equation σ^E is the Poisson's ratio of the material, expressed by $\sigma^E = \frac{S_{12}^E}{S_{11}^E}$, where S_{11}^E and S_{12}^E are elastic compliance with an electric field having a constant intensity. η_1 is a root of the equation:

$$\eta_1 J_0(\eta_1) - (1-\sigma^E) J_1(\eta_1) = 0$$

where J_0 and J_1 are Bessel functions. Piezoelectric ceramic materials generally have a Poisson's ratio σ^E of about 0.3 and therefore η_1 will have a value of 2.05.

Examples of piezoelectric ceramic compositions according to the invention and various physical properties thereof are listed in the following Tables I and II. Table I lists the amounts of the four components $PbTiO_3$, $PbZrO_3$, AO and M_2O_5 in moles and the calcining and sintering temperatures in °C and Table II gives the density in g/cc, dielectric constants ϵ_0 and ϵ_3 respectively before and after electrostatic polarization, planar coupling coefficient k_p and mechanical coefficient Q or Q_m. All the listed examples were prepared in accordance with the method previously described starting with the corresponding raw

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materials and the dielectric constants before and after the electrostatic polarization of the sample and the planar coupling coefficient k_p were measured in the manner above described.

TABLE I

Composition of Present Invention and Treating Temperatures

Group No.	Example No.	Composition				Calcining Temp. in °C	Sintering Temp. in °C
		$PbTiO_3$ in Moles	$PbZrO_3$ in Moles	AO in Moles	M_2O_5 in Moles		
I	1	0.400	0.600	0	0.055 Nb_2O_5	880	1280
	2	0.410	0.590	0	0.055 "	"	"
	3	0.420	0.580	0	0.055 "	"	"
II	4	0.420	0.580	0.030 PbO	0.055 Nb_2O_5	880	1280
	5	0.430	0.570	0.030 "	0.055 "	"	"
	6	0.445	0.555	0.030 "	0.055 "	"	"
III	7	0.420	0.580	0.055 PbO	0.055 Nb_2O_5	880	1280
	8	0.445	0.555	0.055 "	0.055 "	"	"
	9	0.470	0.530	0.055 "	0.055 "	"	"
IV	10	0.445	0.555	0.085 PbO	0.055 Nb_2O_5	880	1280
	11	0.455	0.545	0.085 "	0.055 "	"	"
	12	0.470	0.530	0.085 "	0.055 "	"	"
V	13	0.455	0.545	0.110 PbO	0.055 Nb_2O_5	880	1260
	14	0.470	0.530	0.110 "	0.055 "	"	"
	15	0.480	0.520	0.110 "	0.055 "	"	"
VI	16	0.470	0.530	0.140 PbO	0.055 Nb_2O_5	880	1200
	17	0.490	0.510	0.140 "	0.055 "	"	"
	18	0.510	0.490	0.140 "	0.055 "	"	"
VII	19	0.470	0.530	0.170 PbO	0.055 Nb_2O_5	880	1200
	20	0.490	0.510	0.170 "	0.055 "	"	"
	21	0.510	0.490	0.170 "	0.055 "	"	"
VIII	22	0.390	0.610	0.085 PbO	0.085 Nb_2O_5	880	1280
	23	0.410	0.590	0.085 "	0.085 "	"	"
	24	0.435	0.565	0.085 "	0.085 "	"	"

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TABLE I (Continued)

Group No.	Example No.	Composition				Calcining Temp. in °C	Sintering Temp. in °C
		$PbTiO_3$ in Moles	$PbZrO_3$ in Moles	AO in Moles	M_2O_5 in Moles		
IX	25	0.450	0.550	0.170 PbO	0.085 Nb_2O_5	880	1220
	26	0.460	0.540	0.170 „	0.085 „	„	„
	27	0.470	0.530	0.170 „	0.085 „	„	„
X	28	0.420	0.580	0.055 PbO	0.055 Ta_2O_5	980	1320
	29	0.445	0.555	0.055 „	0.055 „	„	„
	30	0.470	0.530	0.055 „	0.055 „	„	„
XI	31	0.480	0.520	0.110 PbO	0.055 Ta_2O_5	880	1320
	32	0.490	0.510	0.110 „	0.055 „	„	„
	33	0.500	0.500	0.110 „	0.055 „	„	„
XII	34	0.390	0.610	0.085 PbO	0.085 Ta_2O_5	980	1320
	35	0.410	0.590	0.085 „	0.085 „	„	„
	36	0.435	0.565	0.085 „	0.085 „	„	„
XIII	37	0.380	0.620	0.055 CaO	0.055 Nb_2O_5	980	1280
	38	0.400	0.600	0.055 „	0.055 „	„	„
	39	0.420	0.580	0.055 „	0.055 „	„	„
XIV	40	0.400	0.600	0.110 CaO	0.055 Nb_2O_5	880	1250
	41	0.420	0.580	0.110 „	0.055 „	„	„
	42	0.445	0.555	0.110 „	0.055 „	„	„
XV	43	0.400	0.600	0.055 SrO	0.055 Nb_2O_5	980	1280
	44	0.420	0.580	0.055 „	0.055 „	„	„
	45	0.445	0.555	0.055 „	0.055 „	„	„
XVI	46	0.390	0.610	0.085 SrO	0.085 Nb_2O_5	980	1280
	47	0.410	0.590	0.085 „	0.085 „	„	„
	48	0.435	0.565	0.085 „	0.085 „	„	„
XVII	49	0.400	0.600	0.055 BaO	0.055 Nb_2O_5	880	1280
	50	0.420	0.580	0.055 „	0.055 „	„	„
	51	0.445	0.555	0.055 „	0.055 „	„	„

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TABLE 1 (Continued)

Group No.	Example No.	Composition				Calcining Temp. in °C	Sintering Temp. in °C
		$PbTiO_3$ in Moles	$PbZrO_3$ in Moles	AO in Moles	M_2O_5 in Moles		
XVIII	52	0.445	0.555	0.110 BaO	0.055 Nb_2O_5	880	1270
	53	0.465	0.535	0.110 „	0.055 „	„	„
	54	0.490	0.510	0.110 „	0.055 „	„	„
XIX	55	0.365	0.635	0.085 BaO	0.085 Nb_2O_5	880	1280
	56	0.390	0.610	0.085 „	0.085 „	„	„
	57	0.410	0.590	0.085 „	0.085 „	„	„
XX	58	0.420	0.580	0.055 BaO	0.055 Ta_2O_5	980	1320
	59	0.445	0.555	0.055 „	0.055 „	„	„
	60	0.465	0.535	0.055 „	0.055 „	„	„
XXI	61	0.390	0.610	0.085 BaO	0.085 Ta_2O_5	980	1320
	62	0.410	0.590	0.085 „	0.085 „	„	„
	63	0.435	0.565	0.085 „	0.085 „	„	„

TABLE II

Physical Properties of Present Compositions

Group No.	Example No.	Density g/cm³	Dielectric Constant		Planar Coupling	Mechanical
			Before Polar. ε_b	After Polar. ε_a	k_p	Q_m
I	1	7.6	1020	910	0.525	43
	2	7.6	1100	1320	0.540	41
	3	7.6	1230	1480	0.515	39
II	4	7.7	1420	1430	0.605	90
	5	7.7	1540	2090	0.635	82
	6	7.7	1460	1870	0.560	84
III	7	7.6	1100	1040	0.550	106
	8	7.6	1850	2280	0.630	82
	9	7.6	1760	2020	0.570	94
IV	10	7.7	1410	1530	0.580	86
	11	7.7	1550	2410	0.660	75
	12	7.7	1400	2130	0.635	81
V	13	7.7	1360	1160	0.585	92
	14	7.8	1490	1770	0.640	71
	15	7.7	1490	1970	0.635	76
VI	16	7.7	1310	1230	0.560	96
	17	7.8	1280	1790	0.600	100
	18	7.8	1450	1370	0.500	142
VII	19	7.8	1060	935	0.540	93
	20	7.8	1230	1470	0.545	96
	21	7.8	1010	1030	0.540	120
VIII	22	7.6	1020	960	0.345	158
	23	7.6	1050	1310	0.380	120
	24	7.6	940	1000	0.360	115
IX	25	7.5	1180	1120	0.435	123
	26	7.6	1310	1420	0.470	111
	27	7.4	1240	1440	0.440	120
X	28	7.5	1160	1160	0.440	100
	29	7.5	1320	1670	0.505	88
	30	7.5	1250	1470	0.455	106
XI	31	7.8	1550	1740	0.575	82
	32	7.8	1530	1930	0.585	84
	33	7.8	1480	1770	0.550	95
XII	34	7.4	945	830	0.275	144
	35	7.5	1040	1020	0.350	102
	36	7.6	1080	1230	0.320	110
XIII	37	7.5	1740	1650	0.440	114
	38	7.5	1810	2580	0.545	88
	39	7.5	1850	2380	0.510	121

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TABLE II (Continued)

Group No.	Example No.	Density g/cm³	Dielectric Constant		Planar Coupling k_p	Mechanical Q_m
			Before Polar. ε_b	After Polar. ε_a		
XIV	40	7.4	3200	3140	0.560	79
	41	7.3	3050	3500	0.590	85
	42	7.3	2660	2940	0.550	159
XV	43	7.2	1850	2450	0.540	73
	44	7.4	1850	2680	0.580	63
	45	7.3	2240	3250	0.545	77
XVI	46	7.1	3670	3950	0.190	—
	47	7.1	3370	3460	0.220	—
	48	7.2	2800	2790	0.320	91
XVII	49	7.6	1300	1250	0.500	110
	50	7.6	1530	1660	0.545	90
	51	7.5	1640	2450	0.560	80
XVIII	52	7.6	2980	2940	0.600	90
	53	7.6	2320	3150	0.630	80
	54	7.6	1970	2450	0.570	105
XIX	55	7.5	—	2500	0.230	—
	56	7.5	—	2940	0.310	59
	57	7.3	—	2460	0.350	70
XX	58	7.7	2020	2190	0.470	79
	59	7.7	2050	2770	0.510	71
	60	7.7	1940	2430	0.500	92
XXI	61	7.8	2780	2670	0.180	—
	62	7.8	2800	2820	0.220	—
	63	7.8	2530	2680	0.280	—

In the above Tables I and II, Group I is listed only for control purpose and substantially corresponds to a conventional composition composed of the binary lead zirconate-lead titanate system having added thereto niobium pentoxide (Nb_2O_5). The remaining Groups represent specific compositions according to the invention. From Table II it is seen that the compositions of the present invention were significantly improved in planar coupling coefficient and dielectric constant as compared with those of Group 1.

More specifically, the control compositions of Group 1 included 0.055 mole of Nb_2O_5 and varying proportions of $PbTiO_3$ and $PbZrO_3$ totalling 1 mole. In Group 1 0.41 gram atom of titanium rendered the planar coupling coefficient maximum. Examples 1 and 3 illustrate the compositions and physical constants on either side of that composition providing the maximum value of planar coupling coefficient k_p.

The compositions of Group II included 0.055 mole of Nb_2O_5 and 0.03 mole of PbO and varying proportions of $PbTiO_3$ and $PbZrO_3$ totalling 1 mole. The planar coupling coefficient k_p had a maximum value of 0.635 for 0.43 gram atom of titanium. Group II was significantly higher in both planar coupling coefficient and dielectric constant than Group 1.

Group III differed from Group II in that Group III included PbO in an amount of 0.055 mole rather than 0.030 mole. Group III was nearly equal in planar coupling coefficient to Group II but somewhat higher in dielectric constant (ε_a) than Group II.

In Group IV it is noted that Example 11 had the highest values of the planar coupling coefficient k_p and dielectric constant ε_a of Groups I to VII. The PbO component combined with the Nb_2O_5 component can be expressed as $Pb_{m+2}NbO_{3+2.5}$, corresponding to $m=0.75$ in the third term of formula (2).

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That is, the components can be considered to be combined together in a molar ratio of 3 to 2 to provide a singlec omponent. Therefore Group IV corresponds to the composition of a ternary system according to the invention.

Similarly, Group V includes the tertiary component $PbNbO_{3.5}$ or $Pb_2Nb_2O_7$, having the pyrochlore structure, which may be considered to be formed of PbO and Nb_2O_5 in the specified molar amounts. Group V was sintered at 1260°C, which is 20°C less than the sintering temperature for Groups I to IV.

Also, the sintering temperature for Groups VI and VII was still less than that for Group V.

In Groups XIII through XXI the AO component resulted from the corresponding carbonate.

The invention is further illustrated with reference to the accompanying drawings in which:

Figure 1 is a graph plotting certain physical properties against the amount of one component of a quaternary system constructed in accordance with the invention;

Figure 2 is a graphic representation of the quantitative relationship between one of the principal components and the same component as shown in Figure 1 of a quaternary composition in accordance with the invention providing a maximum coefficient of planar coupling; and

Figure 3 is a triangular compositional diagram of materials utilized in the ternary system of the invention.

Referring now to Figure 1, there is illustrated the relationship between the amount of lead oxide (PbO) forming the third term of the formula (1') along the abscissa and the maximum value of the planar coupling coefficient measured in the experiments conducted with Group I through VII for each Group and also the corresponding dielectric constant ϵ_a along the ordinates. The experiments were conducted with the amount of niobium pentoxide (Nb_2O_5) maintained at 0.055 mole. It is noted that the planar coupling coefficient k_p has its maximum value for about 0.09 mole of PbO and that the variation of k_p with PbO content is similar to the variation of the dielectric constant ϵ_a with PbO content. It is to be undersood that a change in amount of Nb_2O_5 leads to a variation in the curves shown in Figure 1.

Figure 2 shows another aspect of the results of the experiments described above. That is, for that composition in each Group providing the maximum value of planar coupling coefficient k_p, the amount in moles of PbO is plotted along the abscissa against the amount of $PbTiO_3$ along the ordinate. From Figure 2 it is seen that the relationship between the amount of the components is substantially rectilinear. This means that, in order to give the planar coupling coefficient a maximum value, a variation in the amount of lead atoms is accompanied by a corresponding variation in the amount of titanium atoms.

While Figures 1 and 2 illustrate the results obtained in terms of lead and titanium respectively, it is to be understood that similar results are obtained in the case of equivalent elements such as calcium and tantalum.

As shown in Figure 3 the piezoelectric ceramic compositions in the form of a ternary system consists essentially of a material selected from the hatched area D E F G H I. In the hatched area, the compositions lying on the line *e f*, that is, including 10 molar percent of $Pb_mNbO_{2.5+m}$ or its equivalent are particularly high in both planar coupling coefficient k_p and dielectric constant ϵ_a.

It has been found to be preferable that the present compositions in the form of a ternary system consist essentially of from 30 to 50 mol % of lead titanate alone or in admixture with an up to equimolecular amount of lead stannate, from 40 to 60 mol % of lead zirconate alone or in admixture with an up to equimolecular amount of lead stannate and from 3 to 15 mol % of a tertiary component of formula $A_mMO_{(2.5+m)}$ where A, M and *m* have the same meaning as above. It is also found to be preferable that the compositions in the form of a quaternary system consist essentially of from 40 to 50 mol percent of lead titanate alone or in admixture with an up to equimolecular amount of lead stannate from 50 to 60 mol percent of lead zirconate alone or in admixture with an up to equimolecular amount of lead stannate from 2.5 to 20% of a tertiary component (AO) and from 2.5 to 10 mol percent of a fourth component Nb_2O_5, Ta_2O_5, Bi_2O_5 or a mixture thereof.

WHAT WE CLAIM IS:—

1. A piezoelectric ceramic composition in the form of a solid solution containing only the components: (1) from 30 to 60 mol % of lead titanate, alone or in admixture with an up to equimolar amount of lead stannate; (2) from 40 to 70 mol % of lead zirconate, alone or in admixture with an up to equimolar amount of lead stannate, components (1) and (2) totalling 100 mol %; (3) from 1 to 30 mol % of PbO, CaO, SrO, BaO or CdO or a mixture thereof; and (4) from 1 to 15 mol % of Nb_2O_5, Ta_2O_5 or Bi_2O_5 or a mixture thereof; the percentages of components (3) and (4) being based on the total of components (1) and (2).

2. A composition according to claim 1, in which the amount of said component (1) is from 40 to 50 mol %, the amount of said component (2) is from 60 to 50 mol %, the amount of said component (3) is from 2.5 to 20 mol % and the amount of said component (4) is from 2.5 to 10 mol %.

3. A piezoelectric ceramic composition in the form of a solid solution containing only the

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components: (1) from 30 to 60 mol % of lead titanate, alone or in admixture with an up to equimolar amount of lead stannate (2) from 25 to 65 mol % of lead zirconate, alone or in admixture with an up to equimolar amount of lead stannate; and (3) from 1 to 30 mol % of a compound of general formula $A_mMO_{2.5+m}$, where A is Pb^{II}, Ca^{II}, Sr^{II}, Ba^{II} or Cd^{II}, M is Nb^{V}, Ta^{V} or Bi^{V} and m is 0.25, 0.50, 0.75, 1.00, 1.25 or 1.50, components (1), (2) and (3) totalling 100 mol %.

4. A composition according to claim 3, containing only from 30 to 50 mol % of said component (1), from 40 to 60 mol % of said component (2) and from 3 to 15 mol % of said component (3).

5. A composition according to claim 1 or claim 3, substantially as hereinbefore described with reference to any one of the foregoing Examples.

6. A composition according to claim 3, substantially as hereinbefore described with reference to Figure 3 of the accompanying drawings.

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Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1972.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

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1291761 COMPLETE SPECIFICATION

2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

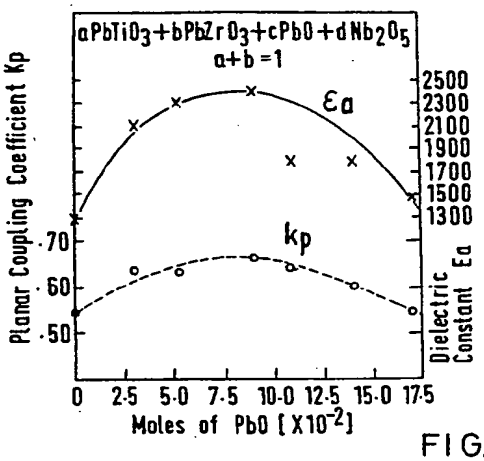

FIG. 1

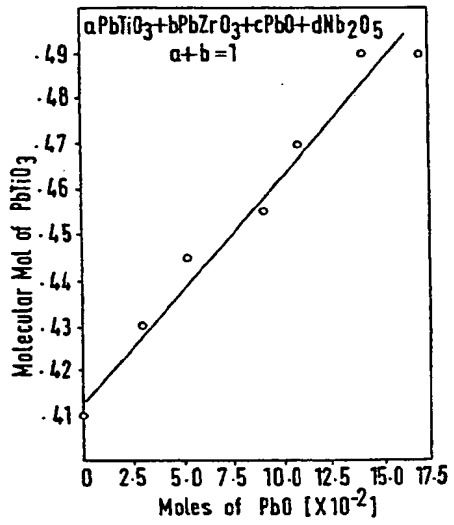

FIG. 2

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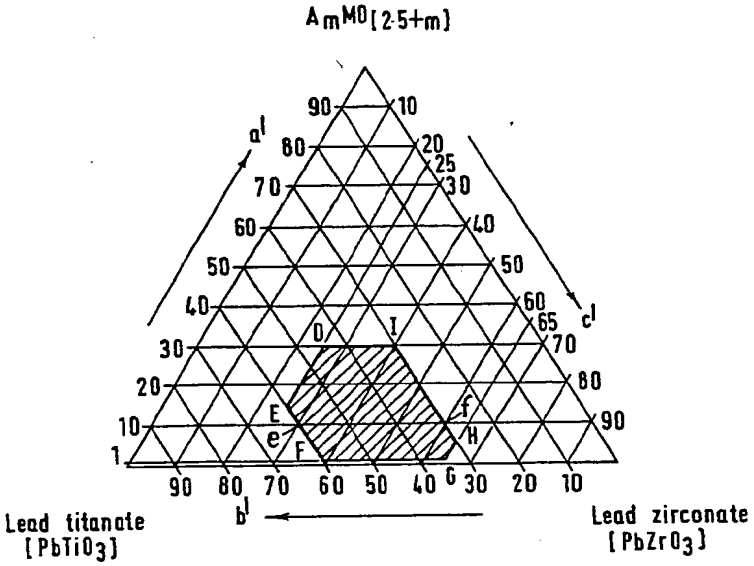

FIG. 3

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